Prediction of the water/oil interfacial tension from molecular simulations using the coarse-grained SAFT-γ Mie force field

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Abstract

This work is framed within the Ninth Industrial Fluid Properties Simulation Challenge, with the aim of assessing the capability of molecular simulation methods and force fields to accurately predict the interfacial tension of oil + water mixtures at high temperatures and pressures. The challenge focused on predicting the liquid-liquid interfacial tension of binary mixtures of dodecane + water, toluene + water and a 50:50 (wt%) mixture of dodecane:toluene + water at 1.825 MPa (250 psig) and temperatures from 110 to 170 °C. In our entry for the challenge, we employed coarse-grained intermolecular models parametrized via a top-down technique in which an accurate equation of state is used to link experimentally observed macroscopic properties of fluids with the force-field parameters. The state-of-the-art version of the statistical associating fluid theory (SAFT) for potentials of variable range as reformulated in terms of the Mie potential is employed here. Interfacial tensions are calculated through a direct method, where an elongated simulation cell is sampled through molecular dynamics in the isobaric-isothermal constant area ensemble ($NP_{zz}AT$). The coarse-grained nature of the force field allows for the accelerated calculation of relatively large systems. The binary interaction parameters that describe the cross-interactions have been obtained in previous works by fitting to interfacial tensions of the constituent binaries at lower pressures and temperatures; these are taken as constant for all conditions and mixtures studied. After disclosure of the challenge results, we observe that the interfacial properties of the mixtures are described with an error of less than 5 mN/m over the whole range of conditions, demonstrating the accuracy and transferability of the top-down SAFT-γ Mie force field approach.

1. Introduction:

The prediction of interfacial tensions (IFT) through molecular simulation is a particularly strenuous test for any force field. Most classical intermolecular potentials are fitted to some limited set of state properties in the homogeneous fluid state (e.g. densities, heats of vaporization, etc.) on the presumption that the parameters obtained will be robust enough and

allow the representation of other thermodynamic state points not employed in the original fitting. This is commonly not the case, thus the prediction of interfacial and transport properties can be employed as a sensitive gauge of the overall performance of a molecular model. It was, with this premise, that the Ninth Industrial Fluid Properties Simulation Challenge was formulated [1]. It was set up with the aim of assessing the capability of molecular simulation methods and force fields to accurately predict the interfacial tension of oil + water mixtures at high temperatures and pressures. The challenge focused on predicting the liquid-liquid interfacial tension of binary mixtures of dodecane + water, toluene + water and a 50:50 (wt%) mixture of dodecane:toluene + water at 1.825 MPa (250 psig) and temperatures from 110 to 170 °C. The disclosure of experimental data after the submission of the entries served to quantify and rank the performance of the several entries.

The fluid-fluid IFT is a key property required in the design of inhomogeneous physical, chemical and biological processes, particularly when the dimensions become microscopic. The IFT plays a key role in determining the free energy barrier for the nucleation of new phases, the mesoscale self-assembly of matter, the transport and diffusion of molecules through fluid interfaces, etc. Its distinctive characteristic is that although it is a property only defined at the interface of a macroscopically inhomogeneous system, its roots can related directly to the underlying molecular forces [2,3,4]. IFT can be readily be obtained from experimental measurements [5, 6] and is frequently generalized in terms of empirical correlations which have a relevant practical application but very restrictive predictive power [7]. Theoretical approaches, on the other hand, are limited in both their predictive approach and the complexity of the systems that can be tackled [8,9]. In this scenario, computer simulations provide the most flexible and fundamental platform for the analysis of molecular interactions and a route to obtaining the IFT of complex fluid mixtures. The reader is referred to Ghoufi *et al.* [10] for a review of the current state of the art in the field.

The output of a molecular simulation depends crucially on the quality of the force field employed. Molecular mechanics force fields usually describe molecules in a fully atomistic way, with multiple parameters describing the charge anisotropy, bond geometries and flexibility and the site-site dispersion interactions. Some compromises must be made in order to maintain the computational effort tractable (e.g. the neglect of quantum effects, the description of charges as fixed points, etc.) and a further level of empirical fitting and adjustment of the dispersion forces is also required, hence the final intermolecular potential will unavoidably have limitations in terms of its capability to model real molecules.

We employ in this work coarse-grained (CG) intermolecular potentials to describe the fluid-fluid interactions. Within this approximation one considers spherical elements that correspond to a chemical moiety comprised of several heavy atoms; *i.e.* "super-atom" beads. Coarse graining methods reduce the number of degrees of freedom in the system, allowing for a more compact

description and a decrease in several orders of magnitude in the computational power required as compared to the more standard all-atom description while retaining a molecular description in terms of the size, shape and average interactions between molecules. Furthermore, CG allows the study of either larger systems, longer time frames and/or shorter simulation runtimes.

2. The SAFT-γ Mie force field

Generalities

The methodology used to parametrize molecular models for simulations is crucial to obtain the required accuracy, representability and transferability. All-atom models are commonly fitted to thermodynamic and structural properties *i.e.* a liquid density, radial distribution function, enthalpy of vaporization, at a particular thermodynamic state point. If the model is physically sound, some degree of transferability to other state points will be achieved. The current rigid water models are a prime example of the difficulties involved in this procedure: it seems a futile task to reproduce all thermodynamic properties with a unique set of parameters [11]. "Bottom-up" parametrizations based on the mapping of CG beads to an equivalent atomistic model will inevitably be of lesser accuracy and transferability than the parent all-atom model. Hence this route should be avoided if one is in search of a force field that is applicable to a wide range of state points. This is the underlying rationale behind the fitting to the full free energy landscape of the fluid: to use a "top-down" approach where the parameters of the model are the best compromise of an effective pair potential best able to reproduce a whole spectrum of thermophysical properties.

For the purpose of linking the thermodynamic properties of a fluid to intermolecular potential, we propose to use an accurate equation of state, namely the Mie version of the statistical associating fluid theory (SAFT). The essence of the SAFT force field is that the potential parameters can be obtained by fitting an equation of state [12,13,14] to macroscopic thermophysical properties of pure substances [15], as the equation of state itself is expressed in terms of parameters that have a one-to-one correspondence with the underlying intermolecular potential. This "top-down" approach not only greatly simplifies the parametrization of the force field, but also and uniquely imparts it with robustness and transferability, as the procedure essentially amounts to fitting the whole free energy landscape of the component with "average" quantities. For the molecules involved in this challenge, the parameters for the pure components have been published previously and are detailed here for completeness.

The molecular model we adopt is that of CG chains of tangent spherical segments, which interact with each other via a particular case, (λ, 6), of the Mie potential:

$$\phi(r) = \left(\frac{\lambda}{\lambda-6}\right)\left(\frac{\lambda}{6}\right)^{6/(\lambda-6)} \varepsilon\left[\left(\frac{\sigma}{r}\right)^{\lambda} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (1)$$

where r is the distance between centers of a pair of beads, ε is the depth of the potential-energy well, λ is the repulsive exponent which defines the range of the potential and σ is the length scale, corresponding to the distance where the potential changes from a repulsive to an attractive nature (which can be interpreted as a segment diameter). Our adoption of the particular Mie (λ,6) form in preference to the general form where both exponents are left as adjustable parameters follows from the observation that, for the description of fluid phase behaviour, the repulsive and attractive exponents are correlated [16]; this correlation reduces the degrees of freedom, thereby allowing the attractive exponent to be fixed to the London-dispersion value of six.

The above described coarse-grained models are top-down approaches, hence inherently do not include explicitly any information on the intramolecular interactions. However, one can recognize that overall shape, intersegment connectivity and rigidity are crucial to preserve the quality of the structure prediction [17]. Within SAFT each molecule is represented by m spherical segments. This adds to the model an additional parameter, m, which quantifies the number of elements in a chain molecule. A limitation of the theory is that the CG segments are rigidly bonded at a distance corresponding to that used to evaluate the reference radial distribution function. In this work, this distance is taken to be the characteristic size, σ, i.e. the CG spheres are rigidly bonded at a distance of σ. The actual geometry of the resulting model, i.e. the number of beads and their connectivity are specified *a priori* by the user with some knowledge of the morphology of the molecule. The SAFT theory lends itself naturally to consider linear chain molecules made of tangentially-bonded beads and more recently to rigid rings [18]. On the bending of longer linear chains, the underlying theory only specifies that, on average, the molecules should remain extended [19], so intramolecular interactions (bending restrictions) must be superimposed on the model.

The SAFT-γ Mie force field and the corresponding equation of state have been incorporated through the use of a density gradient theory to predict the interfacial tensions of fluids analytically [20]. This method, despite being amongst the most accurate correlations available, is essentially based on an equation of state and not on actual molecular modelling; thus it was not deemed to fall within the remit of the challenge and is not discussed further. We stress in ending this section, that although the force fields are inspired and parameterized by an analytical equation of state, the intermolecular potentials are used in classical modeling (in this case, Molecular Dynamics simulations) with no further intervention from the theory.

Pure components

An illustration of the molecular models employed in this work is given in Figure 1.
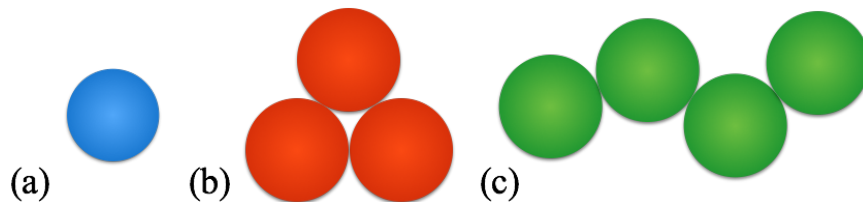
Fig. 1 Coarse-grained models of fluids. (a) water as a single isotropic bead; (b) toluene as a rigid ring trimer; (c) n-dodecane as a tangent chain of four beads. Molecules not shown to scale.

Water is modeled as a single isotropic sphere as described by Lobanova *et al.* [21]. Lobanova suggests three possible models for water. Here we employ the model CGW1-ift of said paper, as it provides for the best representation of interfacial properties. A price to pay for the simplicity inferred by the use of an isotropic model for such a complex molecule such as water is that the parameters of the Mie are necessarily a function of temperature. For the model used, $\lambda = 8$; ε/k_B (K) = (-4.806 x 10^{-4}) T^2 + 0.6107 T + 165.9, and σ (Å) = (-6.455 x 10^{-9}) T^3 + (9.1 x 10^{-6}) T^2 – (4.291 x 10^{-3}) T + 3.543 , where the temperature T is input in K.

Toluene is modeled as a planar ring of three beads rigidly bonded in an equilateral triangular geometry with center-to-center bonds fixed at a distance of 3.6794 Å. Each bead is a Mie bead with, $\lambda = 11.8$; $\varepsilon/k_B = 269.7$ K and $\sigma = 3.6794$ Å. This model was presented by Ervik [22] and the parameters are fitted to the critical temperature, the acentric factor and a given liquid density of toluene. The theory required to parametrize this (and other similar ring molecules) is presented in ref. [18].

The model for dodecane is a chain of four tangentially bonded beads linked by a rigid bond of length 4.351 Å. The model is obtained from a corresponding states parametrization of the SAFT equation of state [23], which provides force field parameters given the knowledge of the critical temperature, the acentric factor and a given liquid density. The parameters for this particular molecule have been described by Herdes *et al.* [24] as $\lambda = 18.41$; $\varepsilon/k_B = 378.56$ K and $\sigma = 4.351$ Å. In the case of the chain fluid, there is a restriction added by an angle bending potential between three consecutive beads, $\psi = k(\theta - \theta_0)^2$ where θ is the angle subtended by three consecutively bonded spheres. The particular values are, $\theta_0 = 157.6°$, and the constant that restricts the distribution is $k = 3.38$ J mol^{-1} deg^{-2} (2.65 kcal mol^{-1} rad^{-2}).

Mixtures

For the case of mixtures, a new set of unknown parameters come into play, namely the cross-parameters corresponding to the binary interactions. The best course of action is to obtain these parameters by fitting them to reproduce the properties of selected mixtures, however, this is seldom possible. Lafitte *et al.* [12] suggested the following combination rules that can be used as a first approximation to describe the interaction between two different Mie fluids, labeled with subscripts *ii* and *jj*.

$$\sigma_{ij} = \frac{\sigma_{ij} + \sigma_{ij}}{2} \quad ; \quad \varepsilon_{ij} = (1 - k_{ij}) \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad ; \quad (\lambda_{ij} - 3) = \sqrt{(\lambda_{ii} - 3)(\lambda_{jj} - 3)} \quad (2)$$

In the Lafitte rules, the provision of a binary interaction parameter, k_{ij}, is built in, which can aid in the fine-tuning of mixture properties. The binary interaction parameters are symmetric, *i.e.* $k_{ij} = k_{ji}$ and independent of composition temperature and/or pressure. For the organic-water interactions, as our models do not explicitly take into account the association effects, a rather large value of k_{ij} is to be expected. We use here the value of $k_{ij} = 0.3205$ reported [25] for the mixture of dodecane + water, (fitted to the interfacial tension of the hexane + water system at 298 K) assuming this as a robust and transferable value. For the water + toluene mixture, Ervik reported a cross-parameter based on the fitting of interfacial tension of water + toluene mixtures at room temperature and atmospheric pressure [22]. For the toluene + dodecane mixture, no deviations from ideality are assumed. A summary of the binary parameters is given in Table 1.

No additional parameters or fitting are employed in the ternary mixtures; only pair-wise binary interaction parameters are taken into account. It should be noted that all CG models and the binary interaction parameters used here had been published in other works before the challenge specification was announced, as it was the purpose of the challenge to evaluate the predictive nature of currently available models, rather than their capacity to correlate and/or extrapolate existing data.

Table 1. Binary interaction parameters, k_{ij} employed in the simulations.

Binary pair	k_{ij}	Ref.
Water + Dodecane	0.3205	25
Water + Toluene	0.241	22
Dodecane + Toluene	0.0	-

3. Molecular simulation details

Interfacial tensions are calculated through a direct method, whereas an elongated simulation cell is sampled through classical molecular dynamics (MD) in the isobaric-isothermal constant area ensemble ($NP_{zz}AT$). Direct coexistence systems are generated using orthorhombic boxes with side dimensions $L_y = L_x = 4.5$ nm and L_z being roughly five times longer. The elongation of the cell, L_z, will vary during the simulation to maintain the specified external pressure, which in this anisotropic geometry corresponds to the diagonal z component of the pressure tensor, P_{zz}. Systems are set up to contain close to 8000 CG beads (see Table 2 for details). Since water molecules are in general smaller than the organic molecules, a larger proportion of the former is used to ensure that the resulting binary systems have approximately the same volume fraction of each of the coexisting liquid phases. For the ternary system this choice corresponds to a larger organic phase volume, which is actually beneficial to resolve the density inhomogeneities associated with the distribution of the organics at the interfaces. Initial systems are set up by separately equilibrating pure fluids and placing them in an elongated box in such a way that two liquid slabs are present face-to-face in the elongated (z) direction. Initial guesses of the system sizes are provided by calculating the densities using the SAFT equation of state.

For the case of the ternary mixture, the direct simulation method employed presents a particular challenge if one is to ensure a pre-determined bulk phase composition. As it is the overall system composition that is constant, if there is a phase split, the components will distribute themselves amongst the phases present to maintain the equality of chemical potential of each component across all phases (diffusive equilibrium). It is not possible to predetermine the coexisting bulk compositions, so the initial system composition has to be chosen by trial and error if one is to fulfill an imposed condition [26]. Employing an overall 50/50 mass ratio of toluene/dodecane in the simulation box leads to an incorrect final bulk composition as the two organics will distribute themselves in different ways amongst the two phases and the interface. In this particular system, the asymmetric distribution of the organics at the interface plays an important role in the mass distribution along the simulation box. Finite size effects play a crucial role in this scenario: the ratio of the interfacial area to the volume of the system scales as $O(1/L)$, where L is a characteristic length. For a large (macroscopic) system, where L scales to infinity, the mass associated with adsorption at the interfacial region is negligible with respect to the bulk mass. However, in a finite sized system, such as the one employed in nanoscopic molecular simulations, the volume occupied and the amount of mass at the interfacial region is a significant proportion of the overall mass. If the compositions at the interfacial regions differ from the bulk phases (*i.e.* there is preferential adsorption at the interface), the interfacial region depletes (or supplies) additional molecules from (to) the bulk phases. Preliminary runs of the mixture system demonstrated that this was indeed the case and an appreciable adsorption of toluene at the interface was to be expected (see next section). We employed the SAFT equation of state coupled to square gradient theory [20] to obtain an estimate of this enhancement and to backtrace the required global compositions for these systems. A simplification may be made if one assumes that the organic composition in the aqueous phase is negligible. Following this

approach, the overall ratio of toluene/dodecane in the ternary system is set at 911/768 weight for all temperatures. The accuracy of this estimate is verified posteriorly by evaluating the overall density ratio in the equilibrated states.

We use the Gromacs version 4.5.5 [27] molecular dynamics suite of programs with no modification to set up the initial systems and for equilibration due to the relative ease of use of the code. We use HOOMD-blue version 1.2.1 [28] with GPU acceleration, through the raaSAFT simulation framework [29,30], for the production runs as it proved to be computationally advantageous, with speedups of a factor of two or more in wallclock times.

The production MD simulations are carried out over a time of $t = 150$ ns, using a timestep of 0.01 ps; the models do not consider electrostatics explicitly and all interactions are short-ranged; hence the intermolecular potential is cutoff at 2 nm with no shifting of energy or force, and no long range corrections are applied. We apply the Berendsen thermostat with a time constant of 1 ps and the Berendsen barostat, affecting only the z dimension of the simulation box with a time constant of 1 ps. The length of the runs guarantees attaining equilibrated states and sufficient configurations to report accurate statistics.

Table 2. Simulation details of the model systems

Mixture: Water +	dodecane	toluene	dodecane:toluene
Number of water molecules (beads)	6525	6525	6525
Number of toluene molecules	-	807	807
Number of toluene beads	-	2421	2421
Number of n-dodecane molecules	368	-	368
Number of n-dodecane beads	1472	-	1472
Box dimension in x and y (fixed)	4.5 nm	4.5 nm	4.5 nm
Box dimension in z (average @ 110°C)	17.92 nm	18.27 nm	25.95 nm

We calculate the interfacial tension using the mechanical route, which requires the evaluation of forces [31] to obtain the average Cartesian components P_{ii} of the pressure tensor

$$\gamma = \frac{1}{2} \int_{-L_z/2}^{L_z/2} \left(P_{zz}(z) - \frac{P_{yy}(z) + P_{xx}(z)}{2} \right) dz$$

(3)

The leading pre-factor of 1/2 implies the presence of two interfaces in our particular case. For the geometry employed in our simulations, the pressure is obtained from $P = P_{zz}$, *i.e.* the component of the pressure tensor normal to the interface. As seen above, the calculation of the IFT relies on the evaluation of the elements of the pressure tensor. These quantities are inherently "noisy" due to the natural fluctuations of the systems and the fact that the tension is calculated as an integral

over a quantity that involves the elements of the tangential pressure (P_{xx} and P_{yy}), which varies by several orders of magnitude across the rather narrow fluid-fluid interface. In this context, long simulations (as compared to those performed with the commonly-employed classical atomistic models) are required to have statistical confidence in the results.

The normal pressure, P_{zz}, in the $NP_{zz}AT$ ensemble, corresponds to the pressure specified by the challenge, namely 250 psig which is equal to 264.7 psia = 18.25 bar = 1.825 MPa. In this type of simulation, the box length (in the z direction) is varied throughout the simulation to maintain the specified pressure.

4. Results

Pure components

For completeness, we present in Figure 2 a comparison of the calculated interfacial tensions of the pure components along the vapor-liquid equilibria temperature range, comparing our simulation results to smoothed experimental data [32]. The quality of the prediction evidences the robustness of the CG model, particularly for the organic phases, where such results are a prediction of the models, as no interfacial properties are used in the model parametrization. Overall error is less than 2% over the whole temperature range.
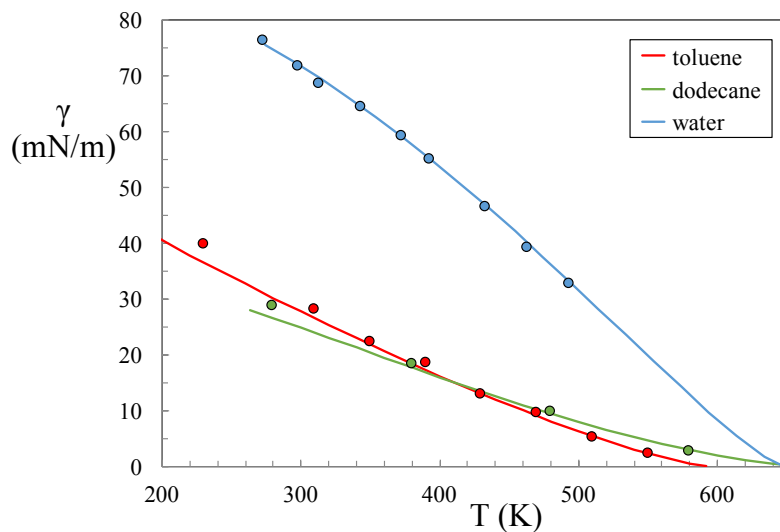

Fig. 2 Comparison of the performance the CG models. Symbols are simulation data for water (blue) [21], toluene (red) and dodecane (green) . Solid lines are smoothed experimental data from ref. [32].

Challenge results

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The systems considered are binary mixtures of water with n-dodecane or toluene, and a ternary mixture of water plus a 50/50 mass basis n-dodecane/toluene mixture (*i.e.* 64.9 mol% in toluene). It is assumed from the onset that the systems are in liquid-liquid equilibria, hence the phase split is independent of the overall mass present initially: there is no influence on the final interfacial tension results from the specification of the total number of oil and water molecules in the system, only the relative amounts of each phase present would change as a result of the final equilibrium composition. The simulation setup is further helped by the fact that the aqueous phase is essentially pure (*c.f.* Figs. 3 and 4). Hence the molecular reordering and eventual equilibration consists of the diffusion of the appropriate number of water molecules into the organic phase. Notwithstanding, to have a sensible bulk phase for both the aqueous and organic phases, the numbers of *beads* are partitioned in the binary systems to guarantee roughly an equal volume between the organic and aqueous phases. A snapshot from a three-component simulation is given in Figure 3. The aqueous phase (right-hand side of Fig. 3) is seen to be virtually pure water while the organic phase (left) has an appreciable amount of water which will depend on the temperature and composition of said phase. As expected, the organic phase has a lower density than the aqueous phase. The interface is very diffuse, spanning about 3 nm and there is evidence of an excess adsorption of toluene at the interface, which is quantitatively confirmed by the density profiles across the interface (Fig. 4). The interface becomes wider and the toluene enrichment less pronounced as the temperature increases and the interfacial tension decreases. These general observations are seen at all temperatures.

The enrichment of the interface by the toluene molecules has also been reported by another of the challenge entries [33] where a much higher fidelity atomistic model was employed. It is gratifying to see such an agreement between these two models as the SAFT parametrization is a thermodynamic (top-down) approach, hence the information provided by the simulations amounts to a prediction of the liquid structure which confirms the robustness of the underlying model.
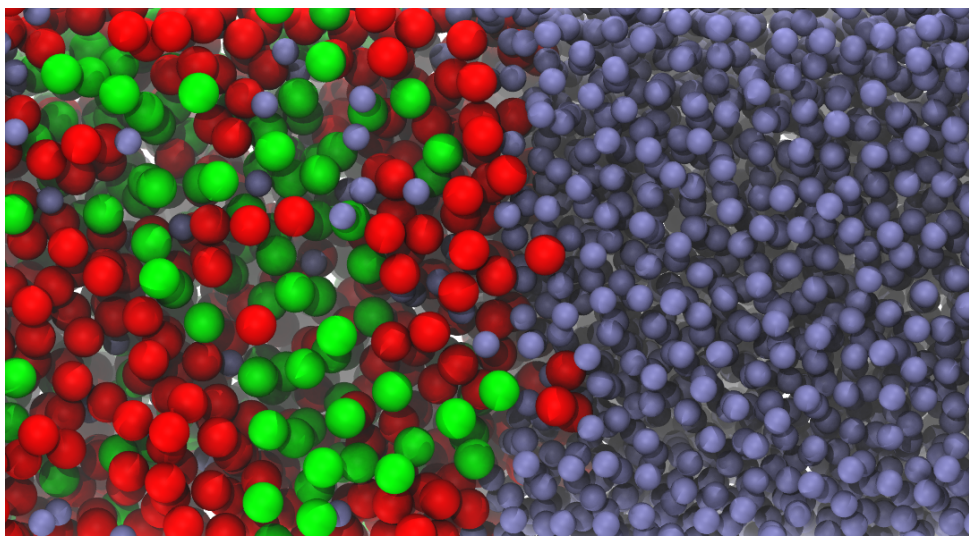
Fig. 3 Snapshot of the detail of the liquid-liquid interface of an equilibrium configuration of the ternary at 130 °C. Water (blue), toluene (red) and dodecane (green). Beads are depicted with a diameter of 0.8σ to aid the visualization.
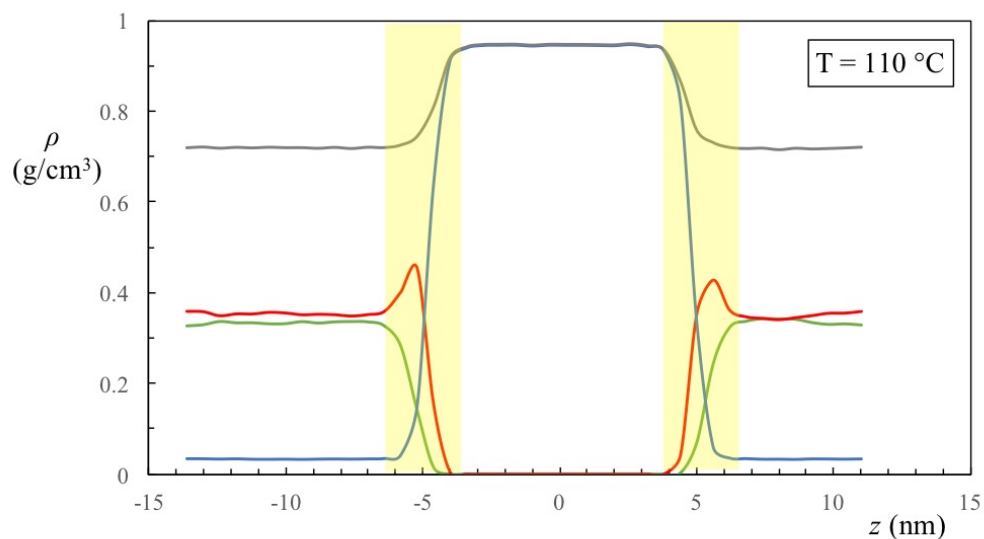

Fig. 4 Average individual component density profile of each component, water (blue), toluene (red), dodecane (green), and total (grey) for the ternary system at 110 °C. Yellow highlights denote the approximate interfacial regions. Distance z is measured in the direction normal to the interface.

Table 3 summarizes the challenge submission alongside the disclosed results. Units are given in mN/m which are numerically equal to dyne/cm. The reported statistical

uncertainties are calculated as the standard deviation of the data, taken every 5 steps and averaged every 1000 steps (10 ps) over at least 5×10^6 steps (50 ns). Average absolute deviations relate to the absolute difference between the simulation and experimental values, normalized by the latter.

Table 3. Interfacial tensions, γ, of systems with water at 250 psig (1.825 MPa). Challenge results (predictions) and comparison to experimental values disclosed after submission. Errors are reported as the difference between the simulation and experimental normalized by the experimental value and expressed in percent. Measurement values in mN/m are numerically equal to those in dyne/cm.

Mixture: Water +	T (°C)	Simulation γ (mN/m)	Experimental γ (mN/m)	error (%)
n-dodecane	110	44.6 ± 0.15	40.0	12
	130	41.4 ± 0.17	36.5	13
	150	37.9 ± 0.19	32.9	15
	170	33.8 ± 0.17	28.5	19
toluene	110	27.5 ± 0.08	28.6	-3.8
	130	25.0 ± 0.04	26.4	-5.3
	150	21.9 ± 0.06	23.8	-8.0
	170	19.1 ± 0.13	20.2	-5.4
n-dodecane : toluene blend	110	33.0 ± 0.23	31.4	5.1
	130	30.0 ± 0.27	29.0	3.4
	150	27.3 ± 0.22	26.1	4.6
	170	24.1 ± 0.08	22.6	6.6

Comparison with experimental data

After the disclosure of the challenge results, we were able to evaluate the accuracy of the predictions made herein. We notice that the water + alkane interfacial tensions were consistently higher than the experimental data by around 5 mN/m on average. In hindsight, it is this binary pair for which there is the largest uncertainty, as several conflicting values of k_{ij} are reported [21,25]. Not only are the experimental alkane-water tension data in conflict with each other as exemplified in ref. [34], but crucially the values of the interaction parameter will depend on the phase (organic or aqueous) and the thermodynamic state involved. On the other hand, toluene + water mixtures were much better represented with a slight underprediction of -1.4 mN/m on average. Consequently, the ternary mixture itself was overpredicted by an average of 1.3 mN/m. It is satisfactory to see that the experimental trends with temperature are followed faithfully. One could arguably re-fit the k_{ij} values to the disclosed results, with the obvious outcome of an even better result (with or without detriment to the underlying liquid-liquid equilibria). We note that

this, however, was not the remit of this work, but rather to quantify the level of confidence that one can place on the currently available molecular models.

The temperature-dependency of the excess adsorption of toluene at the interface will clearly have an influence on the final results, and any higher local concentration at the interface will have a depletion effect on the bulk composition, which is this type of simulation cannot be specified *a priori*, but is an output of the simulation. Table 4 shows the resulting densities of the bulk regions of the ternary mixture, quantifying the deviation from the ideal 50/50 toluene/dodecane mass ratio employed in the experiments. For a given system size, the overall composition needed to reach a 50/50 wt% composition in the organic region seems to be quite independent of temperature. With increasing temperature, the height of the composition enhancement decreases but the interfacial width increases; these two factors seem to largely compensate.

Table 4. Bulk region individual mass densities (compositions) in the organic phase of the water;dodecane:toluene mixture at 250 psig (1.825 MPa).

T (°C)	Density (g/cm^3)		
	Toluene	Dodecane	Water
110	0.352 ± 0.005	0.333 ± 0.004	0.035 ± 0.001
130	0.331 ± 0.007	0.320 ± 0.007	0.042 ± 0.001
150	0.310 ± 0.006	0.298 ± 0.005	0.051 ± 0.001
170	0.291 ± 0.007	0.270 ± 0.010	0.061 ± 0.004

5. Conclusions and observations

We have presented a prediction of the interfacial tensions of binary and ternary aqueous mixtures of oils obtained by molecular simulations of coarse-grained model of fluids, parametrized via a top-down or thermodynamic route. The results attained from the blind test reveal that the SAFT-based CG models are both robust and representative, having a similar and/or higher accuracy than the atomistically-detailed models [35].

The experimental results for the IFT of the mixture show that they are consistently lower (by 3 % on average) than what would be expected by a simple molar average of the tension of the pure

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toluene/water and dodecane/water binaries at the same temperature. This observation has been reported previously [36] as a conclusion of a molecular simulation study of oil/water systems employing atomistically-detailed force fields. Since the aromatic/water interfacial tension is in general lower than the corresponding alkane/water tension, the lower mixture tension is presumed to be driven by an accumulation of aromatics at the interface. Density profiles across the interface reported in [36] (which agree with the ones we present here) confirm this observation. Clearly the excess adsorption of the aromatics is a key prediction of the CG model and confirms the robustness of the SAFT force field.

The reliance on rather large binary interaction parameters between the organics and water denounce the intermolecular potential for water as being far from satisfactory. We believe that it is here, in the description of the water molecule and its interactions with organic fluids, that the largest discrepancies with the experimental results arise. There is scope to improve the current SAFT CG models for associating mixtures. In particular, explicitly considering the associating nature of water is a crucial step forward. SAFT has a built-in provision for embedding associating sites onto the models, which has not yet been employed in CG models, although there is no fundamental limitation for this. Work in this area is actively pursued by our group.

5. Acknowledgements

HOOMD-blue computer files required to reproduce for all mixture simulations reported in this article can be accessed on Figshare at https://dx.doi.org/10.6084/m9.figshare.4685485 and used under the Creative Commons Attribution license.

6. References

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